

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to the Production of Non Caking Common Salt

We, A. & R. SCOTT LIMITED, a British Company of West Mills, Colinton, Edinburgh, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improvements in or relating to the production of sodium chloride having a low tendency to caking in moist atmosphere.

When crystalline sodium chloride is stored in contact with air, it is generally found that the crystals agglomerate or cake and, where this condition is undesirable, the caked salt has to be subjected to a further processing. This tendency to caking is more pronounced in humid atmospheres and may also be affected by temperature, pressure and storage time.

Caking is generally recognised as depending largely on the crystalline nature of the salt, since an increase in the size and uniformity of the grains is found to reduce the tendency and cubic salt formed by crystallisation from deep solutions has notably more tendency to cake than, for example, pan salt which is formed on the brine surface.

We have found that the tendency of cubic-crystalline sodium chloride to caking may be reduced in particular advantageous manner if certain iron complexes are added to the solid crystalline salt.

According to the present invention, therefore, we provide a process for reducing the caking tendency of crystalline sodium chloride in which there is added to cubically-crystalline sodium chloride one or more complex compounds of iron in which the iron is complexed by bonding through an oxygen atom or atoms with an aliphatic compound having 3 to 6 carbon atoms and containing

two or more carboxyl groups together with one or more hydroxyl groups.

Tartaric acid citric acid and gluconic acid are preferred examples of complex forming compounds. Complex compounds of iron are generally in the form of an iron atom bonded to six functions although two or more functions may be supplied by single molecules e.g. citric acid etc. Where the number of acidic, for example carboxylic, functions is in excess of the valency of the iron, the excess, in neutral compounds, is neutralised by a basic atom or molecule such as an alkali or alkaline earth metal atom or, preferably, an ammonium radical. Thus, for example, where the iron is in the trivalent state, as is preferred, and six carboxyl groups are bonded to the iron atom, three monovalent cations or an appropriate number of cations of other valencies will be present. Examples of preferred compounds for addition to salt according to the invention include ammonium ferric citrate, ammonium ferric tartrate and ammonium ferric gluconate.

The additive should preferably be distributed as uniformly as possible over the total crystal surface of the salt since in this way a minimal quantity of the compound will produce the desired effect. For this reason, it is convenient to add an aqueous solution of the additive to the crystalline sodium chloride and this can advantageously be carried out either by atomising the solution onto salt which has been separated from the mother liquor, and is either in the wet or dry state, or by adding the additive to the crystalline salt while still suspended in the mother liquor followed by any convenient separation process.

The additive used according to the invention can, as stated above, be employed in extremely small quantities so that salt of reduced caking tendency may be obtained in

[Price]

- high purity. In general, there is an optimum quantity of the additive required to produce the maximum effect in a given weight of salt, although this is found to vary to some extent with the grain size of the salt crystals. For salt of crystal size approximately 0.3 mm., we have found that these optimum quantities lie generally between 0.0001 and 0.002% of the weight of sodium chloride. In many cases, quantities of the additive as low as 0.00002% may be effective in reducing caking where storage conditions are favourable, although with very low percentages it is essential that the additive be uniformly distributed over the total crystal surface of the salt. Indeed, if uniform distribution is not obtained, increased quantities of the additive may be necessary.
- When the quantity of the additive per unit crystal surface is calculated, it is rather surprisingly found that, if completely uniform coverage were possible, there is often insufficient adsorbed material to cover completely the crystals with a mono-molecular crystalline layer. In other words, since completely uniform coverage is scarcely attainable, the crystal surface is not necessarily completely covered by the added compound.
- A major advantage of the present process is that, since the compounds employed are water-soluble, the salt, on dissolution in water, gives a clear solution.
- The salt produced by the present process, although possessing a reducing tendency to caking, may not necessarily be sufficiently free-flowing and it is, therefore, often advantageous to add to salt prepared by the present process one or more of the customary salt additives, for example, magnesium carbonate.
- In order that the invention may be well understood, we give the following examples by way of illustration only:—
- EXAMPLE 1.**
- A stream of salt at 80°, moisture content of 0.1% and mean grain size of 0.01", is fed through a worm conveyor at a rate of 10 tons per hour and a 2.0% solution of ammonium ferric citrate is atomised onto the stream at a rate of 1.7 gallons per hour. The salt is then cooled and dried. The average content of ammonium ferric citrate is 15 parts per million.
- EXAMPLE 2.**
- A 2% solution of ammonium ferric citrate is atomised at a rate of 0.4 gallons per hour onto a stream of cold, dry salt fed through a worm conveyor at a rate of 2 tons per hour.
- WHAT WE CLAIM IS:—**
1. A process for reducing the caking tendency of crystalline sodium chloride in which there is added to cubically crystalline sodium chloride one or more complex compounds of iron in which the iron is complexed by bonding through an oxygen atom or atoms with a saturated aliphatic compound having from 3 to 6 carbon atoms and containing two or more carboxyl groups together with one or more hydroxyl groups. 65
 2. A process as claimed in Claim 1 in which the aliphatic compound is tartaric, citric or gluconic acid. 70
 3. A process as claimed in Claim 1 or Claim 2 in which the iron is in the trivalent state. 75
 4. A process as claimed in any of the preceding claims in which, where the number of acidic groups present in the complex salt exceeds the valency of the iron, the excess acidic groups are in salt-form with basic atoms or radicals. 80
 5. A process as claimed in Claim 4 in which the basic radicals are ammonium radicals. 85
 6. A process as claimed in any of the preceding claims in which the complex compound of iron is one or more of ammonium ferric citrate, ammonium ferric tartrate and ammonium ferric gluconate. 90
 7. A process as claimed in any of the preceding claims in which the complex compound is added to the crystalline sodium chloride in the form of an aqueous solution. 95
 8. A process as claimed in any of the preceding claims in which the quantity of complex compound added is such that its concentration in the dry sodium chloride is not less than 0.00002% by weight. 100
 9. A process as claimed in Claim 8 in which the quantity of complex compound is such that the concentration in the sodium chloride is 0.0001% to 0.002%, the average crystal size of the sodium chloride being approximately 0.3 mm. 110
 10. A process as claimed in Claim 1 substantially as herein described. 115
 11. A process as claimed in Claim 1 substantially as herein defined with reference to either of the examples. 120
 12. Crystalline sodium chloride whenever produced by a process as claimed in any of the preceding claims. 125
 13. Cubically crystalline sodium chloride the crystals of which carry at the surface one or more complex compounds of iron in which the iron is complexed by bonding through an oxygen atom or atoms with an aliphatic compound having 3 to 6 carbon atoms and containing two or more carboxyl groups together with one or more hydroxyl groups. 130
 14. Crystalline sodium chloride as claimed in Claim 13 in which the organic compound is tartaric, citric or gluconic acid. 135
 15. Crystalline sodium chloride as claimed in either of Claims 13 or 14 in which the complex salt is an ammonium ferric complex salt of a carboxylic acid. 140
 16. Crystalline sodium chloride as claimed in Claim 15 in which the complex salt is ammonium ferric tartrate, citrate or gluconate. 145
 17. Crystalline sodium chloride as claimed in any of Claims 13 to 16 in which the com-

plex salt comprises at least 0.00002% by weight of the sodium chloride.

5 18. Crystalline sodium chloride as claimed in any of Claims 13 to 17, the average crystal size of which is approximately 0.3 mm. the complex salt comprising 0.001 to 0.002% by weight of the sodium chloride.

19. Crystalline sodium chloride as claimed in Claim 13 substantially as herein described.

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PROVISIONAL SPECIFICATION

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10 We, A. & R. SCOTT LIMITED, a British Company of West Mills, Colinton, Edinburgh, do hereby declare this invention to be described in the following statement:—

This invention is concerned with improvements in or relating to the production of sodium chloride having a low tendency to caking in moist atmosphere.

When crystalline sodium chloride is stored in contact with air, it is generally found that the crystals agglomerate or cake so that the product is no longer particulate and, where this property is undesirable, the caked salt has to be subjected to further processing. This tendency to caking is more pronounced in humid atmospheres and may also be affected by temperature, pressure and storage time.

Caking is generally recognised as depending largely on the crystalline nature of the salt, since an increase in the size and uniformity of the grains is found to reduce the tendency and cubic salt formed by crystallisation from deep solutions has notably more tendency to cake than, for example, pan salt which is formed on the brine surface.

35 We have found that the tendency of cubically crystalline sodium chloride to caking may be reduced if certain suitable additives are added to the solid crystalline salt.

According to the present invention, therefore, we provide a process for reducing the caking tendency of cubically crystalline sodium chloride in which one or more suitable additives as herein after defined is added to the solid salt.

45 The term "suitable additives" as used in the present specification means compounds of the following types:—

1. Complex salts of iron in which the iron is complexed by bonding to an oxygen atom or atoms.

50 2. Salts of the formulae

$M_x[V(CN)_5]NO$

$M_x[Cr(CN)_5]NO$

$M_x[Mo^V(CN)_5(OH)_2]NO$

55 $M_x[Co(CN)_5]_2$

Wherein M is an alkali metal or ammonia ion. Preferred additives of type 1 are ammonium ferric citrate, ferric ammonium tartrate, ferric ammonium sucrate, ferric ammonium gluconate. Preferred additives of type two are those of the stated formulae wherein

M is sodium or potassium particularly the compounds:—

$K_xV(CN)_5NOH_2O$ (J.C.S. 1959, 1632)
65
 $K_xCr(CN)_5NOH_2O$ (J.C.S. 1959, 872)
 $K_xMo^V(CN)_5(OH)_2NO$ (J.C.S. 1959, 872)

and

$K_x[Co(CN)_5]_2$ (J.A.C.S. 1951, 73, 5710).
The additive should preferably be distributed as uniformly as possible over the total crystal surface of the salt since in this way a minimal quantity of the compound will produce the desired effect. For this reason, it is convenient to add an aqueous solution of the additive to the crystalline sodium chloride and this can advantageously be carried out either by atomising the solution onto salt which has been separated from the mother liquor, and is either in the wet or dry state, or by adding the additive to the crystalline salt while still suspended in the mother liquor followed by any convenient separation process.

The additives used according to the invention can, as stated above, be employed in extremely small quantities so that salt of reduced caking tendency may be obtained in high purity. In general, there is an optimum quantity of the additive required to produce the maximum effect in a given weight of salt, although this is found to vary to some extent with the grain size of the salt crystals. For salt of crystal size about 0.3 mm., we have found that these optimum quantities lie generally between 0.0001 and 0.002% of the weight of sodium chloride. In many cases, quantities of the additive as low as 0.00002% may be effective in reducing caking where storage conditions are favourable, although with very low percentages it is essential that the additive be uniformly distributed over the total crystal surface of the salt. Indeed, if uniform distribution is not obtained, increased quantities of the additive may be necessary.

When the quantity of the additive per unit crystal surface is calculated, it is rather surprisingly found that, if completely uniform coverage were possible, there is often insufficient adsorbed material to cover completely the crystals with a mono-molecular crystalline layer. In other words, since completely uniform coverage is scarcely attainable, the crys-

tal surface is not necessarily completely covered by the added compound.

5 A major advantage of the present process is that, since the compounds employed are water-soluble, the salt, on dissolution in water, gives a clear solution.

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15 In order that the invention may be well understood, we give the following examples by way of illustration only:—

EXAMPLE 1.

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of 0.1% and mean grain size of 0.01", is fed through a worm conveyor at a rate of 10 tons per hour and an 2.0% solution of ammonium ferric citrate is atomised onto the stream at a rate of 1.7 gallons per hour. The salt is then cooled and dried. The average contents of ammonium ferric citrate is 15 parts per million.

EXAMPLE 2.

A 2% solution of $K_2V(CN)_5NOH \cdot O$ is atomised at a rate of 0.4 gallons per hour onto a stream of cold dry salt fed through a worm conveyor at a rate of 2 tons per hour.

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